TAB A

SECRET
(When Filled In)

007073/1

R & D CATALOG FORM

DATE 13 June 1966

1. PROJECT TITLE/CODE NAME
Photo Bleach Photography

2. SHORT PROJECT DESCRIPTION
A follow-on study directed twoard producing a non-silver photographic duplicating material to replace conventional wet silver-halide systems.

3. CONTRACTOR NAME / 4. LOCATION OF CONTRACTOR
[redacted] 25X1

5. CLASS OF CONTRACTOR
Manufacturer

6. TYPE OF CONTRACT

7. FUNDS

FY 19	$
FY 1967	[redacted]
FY 1968	

25X1

8. REQUISITION NO.

9. BUDGET PROJECT NO.
NP-R-1-7073

10. EFFECTIVE CONTRACT DATE (Begin - end)

11. SECURITY CLASS.
AA-Confidential
T-Unclassified
W-Unclassified

12. RESPONSIBLE DIRECTORATE/OFFICE/PROJECT OFFICER TELEPHONE EXTENSION
DDI/NPIC/P&DS [redacted] 25X1

13. REQUIREMENT/AUTHORITY
Required as a dry, immediate-readout photographic medium to replace the cumbersome, time-consuming, conventional silver processes.

14. TYPE OF WORK TO BE DONE
Applied Research

15. CATEGORIES OF EFFORT

MAJOR CATEGORY	SUB-CATEGORIES
Reproduction Techniques & Materials	Dry Film

16. END ITEM OR SERVICES FROM THIS CONTRACT/IMPROVEMENT OVER CURRENT SYSTEM, EQUIPMENT, ETC.
Monthly reports and a final report.

17. SUPPORTING OR RELATED CONTRACTS *(Agency & Other)*/COORDINATION
Project has been coordinated with Army, Navy, AF, and DOD.

18. DESCRIPTION OF INTELLIGENCE REQUIREMENT AND DETAILED TECHNICAL DESCRIPTION OF PROJECT *(Continue on additional page if required)*

This is a continuation of an effort to produce a completely dry, black-and-white, continuous-tone photographic system that overcomes the recognized objectionable features of conventional silver-halide systems. The process currently under study is a polymer system containing components in molecular form which are capable of forming a colored dye image by electro-chemical reaction when exposed to light and rapid heat.

19. APPROVED BY AND DATE

OFFICE	DEPUTY DIRECTOR	DDCI

TAB B

TECHNICAL SPECIFICATIONS

Photobleach Photography is a process in which a dye or mixture of dyes, in combination with a photosensitive agent, bleach or change color upon exposure to light. The process is dry, non-reversible and results in continuous tone, high resolution images. Since the dyes are bleached by light, positive images of positive transparencies are obtained. Heating fixes the film so that it is no longer sensitive to light.

The objectives originally proposed for this process were those to have been achieved ultimately in a long range program of research and development. More recently, a more limited set of specifications have been established based on the properties immediately desirable in a practical, useful film, and on the experience derived during the previous course of the program.

The now established goals to be attained are as follows:

1. Black and white (or colorless) film, with D_{max} = 2.0 or more, over the visible region, and D_{min} = 0.1 or less.

2. Resolution capability of 200 lines/mm.

3. Response latitude of at least eleven steps of a standard step wedge.

4. Sensitivity such that a 4 x 5 copy can be made in 30 seconds or less, using a total power of 1100 watts for exposure and all associated equipment.

5. Ability to control the photographic characteristic curve and thereby vary gamma from 1.0 to 2.0.

6. Ability to utilize a variety of substrates for the photosensitive film, e.g. glass, flexible transparent tape with stability comparable to Mylar, and paper.

7. Fixing time of one minute or less.

8. Storage stability for a period of a year before exposure and six months after exposure.

9. Short time stability to room lights before exposure and/or fixing to eliminate dark room procedures.

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DETAILED OBJECTIVES

The primary goal of this Phase of the program will be to develop a film meeting all of the listed specifications simultaneously. In order to do this, three problems remain to be solved. The first, derivation of a black and white film of appropriate D_{min} and D_{max}, is expected before, or very early in the program. Most of the effort will therefore be limited to the other problems, i.e., very rapid fixing without loss of resolution and without damage to flexible film substrates, control of contrast, and the combination of all the desired properties in one photosensitive film.

A. Film Fixing. The materials developed to date are not suitable for rapid fixing. Temperatures necessary for one minute fixing degrade resolution and produce distortion in these materials. The materials can be modified in several ways in order to obviate the problem. Materials which avoid the necessity for fixing present the most promising approach. In this method, photosensitive agent-dye combinations are used which are sensitive only to ultraviolet light, and not to wavelengths found in common sources of illumination.

Another approach is to midify the fixing technique by using vacuum, forced hot air, pulse heating, infrared heating, or similar means. A third approach is to build into the film a chemical system that reacts with the photosensitive agent and deactivates it upon exposure to infrared, heat or some other post-exposure treatment. Finally, the use of thermosetting resins may reduce the undesirable effects of heat fixing to the required degree.

A simultaneous attack on each of these approaches to the solution of the fixing problem is proposed. Each will account for approximately

10-20% of the total effort. The approaches, mentioned above, are:

1. films sensitive to ultraviolet light only;

2. modification of present heat fixing technique by use of auxiliary techniques: vacuum, forced draft, etc.;

3. modification of materials so as to reduce undesirable effects of heat fixing.

Each of these approaches will be discussed below.

1. <u>Films insensitive to white light</u>. The primary effort thus far has been on films which are sensitive to white light. In order to avoid fixing problems, films sensitive only to ultraviolet would be useful. Two approaches will be taken. In the first, photosensitive agents will be sought which are transparent to visible light and which have sufficiently high bond strength so that visible light will not affect them.

A second approach is to develop the azide process discovered in the sprint of 1966. In this process, inorganic azides are illuminated and ultraviolet light and produce a base which then reacts with appropriate dyes, bleaching them. This is entirely analogous to the bleaching by acid which occurs with some dyes in the halide process. The main advantages of the azide process are that:

a. The bleached form of the one dye with which this process has been tried was more colorless (had a lower and more uniform D_{min}) than any film yet produced by the usual process.

b. A large number of dyes previously ignored because of insolubility can be examined, because the azides used are water soluble, and none of the other photosensitive agents are.

c. The azides are completely inert to light above about 3000A^{o}.

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The disadvantages are:

a. Considerable effort will be needed to find compatible and photographically useful polymer systems for these materials.

b. They may prove to be photographically slow.

c. A mercury light source would be needed, with its attendant inconvenience, or perhaps a powerful xenon flash unit.

2. <u>Modification of heat fixing techniques</u>. If the rate determining step for heat fixing is the diffusion of photosensitive agent through the polymer matrix to the surface, there is probably not much that can be done to improve the speed and effectiveness of heat fixing. If, however, heat fixing is a deactivation by reaction with oxygen or with polymer or if a reaction of some sort (a "fixing reaction") can be initiated by heat but not by ultraviolet and/or visible light, then heat fixing can be made rapid and effective simultaneously by environmental manipulation. A search for a fixing reaction is a large undertaking, and will not be attempted except as a peripheral activity. It does seem worthshile, however, to attempt to improve theefficiency of heat locking by means of forced warm air and by investigating the effect of oxygen and of selected additives on heat locking.

3. <u>Modification of materials</u>. High temperature heat fixing affects dimensional stability and resolution. Polymers exist which show much greater dimensional stability to high temperatures than those which have been investigated. One such ~~ply~~ polymer is polyphenylene oxide, PPO. These polymers will be investigated both as a medium for carrying the dye-OSA combination, and as a flexible substrate to be coated. Coatings must be made as thin as feasible, since fixing time at a given temperature is expected to vary exponentially with film thickness. Thus, high temperature polymers which are also good solvents for the dye-PSA systems are needed.

B. <u>Contrast Control</u>. Recent experiments have indicated that the sensitivity of photobleach films is markedly increased when they are illuminated while warm. In one experiment the sensitivity was increased by ten times for a temperature rise of about 40 degrees above ambient. These results point to a method for controlling contrast. The data are not yet sufficiently quantitative for an accurate estimate of the control available.

Theoretical considerations indicate, and some experiments performed seem to bear this out, and all photobleach materials will have similar H&D curves (Density D versus long Exposure E), differing only with respect to displacement along the log E axis. A single material, at different temperatures, should also have similarly displaced parallel H&D curves. As temperature is raised, the curve is displaced to lower log E values. If, however, temperature is changed during exposure, the shape of the curve will be changed, and hence the slope (or gamma) will be changed also. If the material is heated during exposure, thus increasing sensitivity, the slope will increase and conversely, cooling during exposure will decrease the slope. The measured slopes of photobleach materials are 0.9 to 1.0, with sign opposite to that of silver halide materials. This means that heating during exposure will be the preferred mode, and fortunately, is experimentally easier than controlled cooling.

The objective of contrast control is to render visible distinctions between images with small optical density differences. Another way of achieving this using photobleach materials is to overexpose, when the desired detail is in areas of high optical density, and underexpose in areas of low optical density. For example, a rough calculation indicates that areas of the original of optical density 1,70 and 1.71 can be rendered in the photobleach copy as 1.00 and 1.025 by an overexposure of

25 times. This renders a 0.6% difference of density into a 2.5% difference. Although any portions of the original with a density below 1.2 to 1.4 will be washed out, the contrast on the shadow area will be increased by a factor of four.

It is proposed to allot 30% of the effort of this program to contrast control, the major portion of this time to the technique of varying gamma by varying the temperature, and a minor effort to ascertaining the parameters for over or underexposure. Heating techniques to be ~~xxxx~~ investigated will include two or more of: infrared, conductive heating, induction heating or radio frequency heating.

C. Final Film Formulation. The end product should be a film which simultaneously meets or comes close to meeting all nine of the listed requirements. It is apparent that changes made to improve one characteristic may affect the accomplishments made on another property, either favorably or adversely. The detailed design of the final film will depend on the technique adopted for the solution of the fixing problem. For this reason, the major effort in the first half of the program year will be spent on the three approaches to fixing. When a decision has been made on the approach to be used, work will proceed on the choice of materials to optimize the properties of the over-all film. It is expected that the design of the film will be sufficiently definitive at the mid-point of the program for initiation of the design of the apparatus to be used with these materials.

The final film will be available, at the user's choice, on flexible substrates or on glass plates. A printing paper will also be availab.e However, since paper materials have a low priority in this program, they may not be as satisfactory as the transparent materials.

D. Technical Summary. The work to be done is to be apportioned as follows:

1. Fixing - approximately 45%

   a. system insensitive to white light

   b. heat fixing techniques

   c. high temperature materials

2. Contrast Control - approximately 30%

   a. gamma control

   b. exposure control

3. Film Optimization - 25%

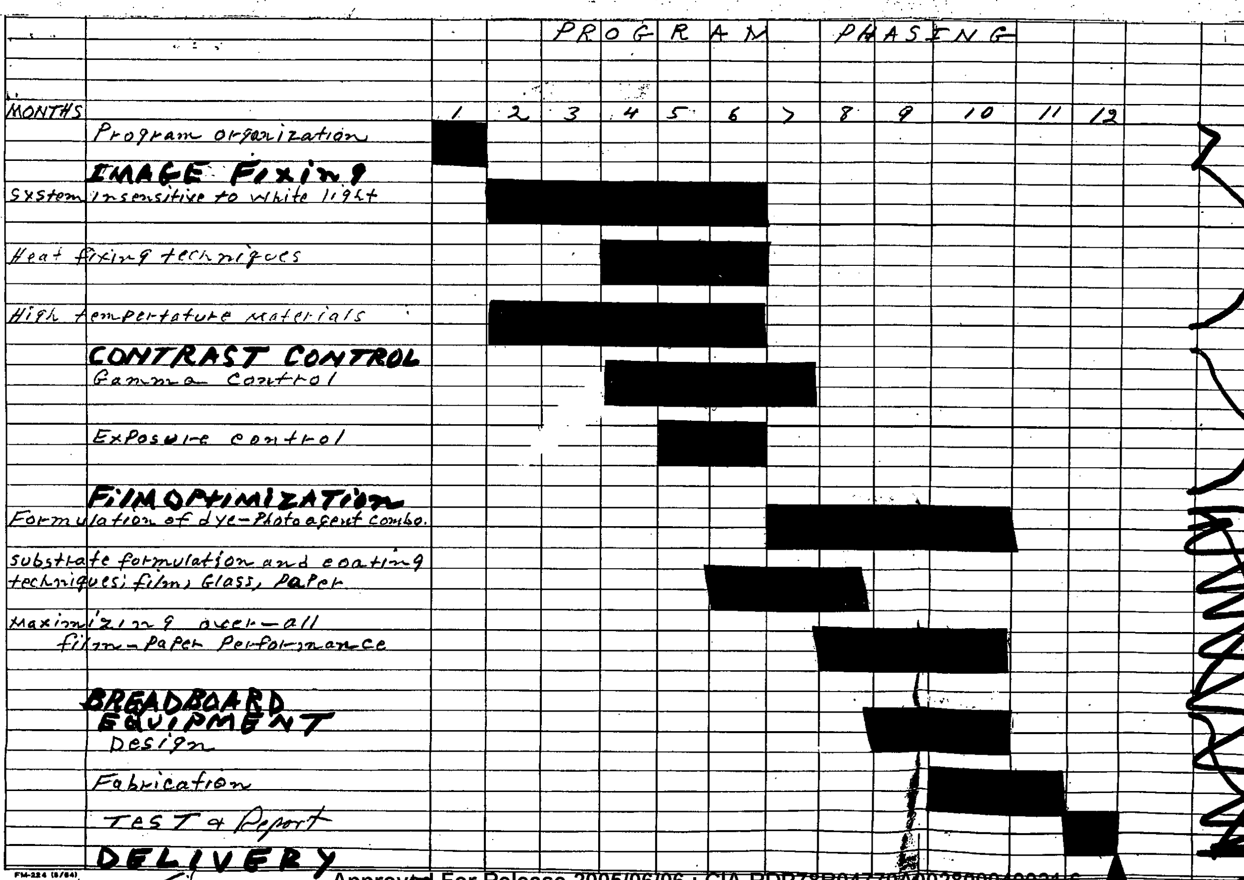
   a. continuing improvements in dye and photosensitive agent combinations

   b. improvements in substrate: polymer formulation, tape and glass coating techniques, papers

   c. maximizing of over-all film performance

25X1

TAB ED



FM-224 (8/64)

DDS/DB TYPING SLIP

Subject: Photo Bleach Photography

Classification: Secret   Project No. 10017

Originator: [redacted]   Date 8-26-66

25X1

	Initials	Date
___(1) Unit Leader		
___(2) Type Rough	CKC	29 Aug 66
___(3) Section Chief	RVJ	29 Aug 66
___(4) Chief, DB	R	
___(5) Asst. for P&DS		
___(6) Originator		
___(7) Type Smooth	CKC	2 Sept 66
___(8) Section Chief	RVJ	2 Sept 66
___(9) Chief, DB	R	
___(10) Asst. for P&DS		

Date of Final Disposition: 7 SEP 1966

File Copy:

✓ (1) Deputy Chief, DB		
___(2) Originator		
___(3) Section Chief		
___(4) Secretary (For filing)		

REMARKS: